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# The unoccupied electronic structure of the semi-conducting room temperature molecular magnet $V(\text{TCNE})_2$

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## Abstract

The unoccupied electronic structure of the organic-based magnet  $V(\text{TCNE})_x$  (TCNE = tetracyanoethylene,  $x \sim 2$ ) has been studied with near edge x-ray absorption fine structure (NEXAFS) and with photoelectron spectroscopy (PES). By studying  $V(\text{TCNE})_x$  upon sodium-doping, the electron-accepting state, i.e. the lowest unoccupied molecular orbital (LUMO) of  $V(\text{TCNE})_x$  was shown mainly to be localized on  $(\text{TCNE})^-$ -units in contrast to the hole-accepting state, i.e. the highest occupied molecular orbital (HOMO), which previously was assigned primarily to be  $V(3d)$ -derived. This study also showed that there are trap states for electron transport located below the  $(\text{TCNE})^{2-}$  level, likely leading to decreased electron mobility.

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## Introduction

Molecule-based magnets possess advantages over their metallic counterparts due to properties such as low density, less energy intensive production, flexibility etc. Their most attractive feature is probably that their properties can be designed by chemical synthesis [1]. Metal-tetracyanoethylene,  $M(\text{TCNE})_x$ ,  $x \sim 2$ , where  $M = \text{V}, \text{Fe}, \text{Mn}$  etc. [2-4] or mixtures of such metals [5,6], is a family of molecule-based magnets with relatively high magnetic ordering temperatures.  $\text{V}(\text{TCNE})_x$  prepared in dichloromethane or by chemical vapor deposition, exhibit a Curie temperature above room temperature,  $T_C \sim 400 \text{ K}$  [7,8], and this, in combination with semi-conducting behavior makes  $\text{V}(\text{TCNE})_x$  a potential prototype material in spintronic (spin-based electronic) [9,10] devices.

Though the magnetic and electric (transport) response of  $\text{V}(\text{TCNE})_x$  has been characterized [8,11], the electronic structure of the material was until recently unknown [12-14]. This has greatly hampered the development of this class of magnets since knowledge about the frontier occupied and unoccupied molecular orbitals are of crucial importance to the electronic and magnetic properties. Furthermore, to correctly understand the (spin-polarized) injection and transport of electrons and holes, the electron/hole accepting and transporting levels of the material must be known. Prigodin *et al* [11] showed that  $\text{V}(\text{TCNE})_x$  exhibits positive magnetoresistance and suggested an electronic structure of  $\text{V}(\text{TCNE})_x$  where the  $(\text{TCNE})^- \pi^*$ -band is split into two subbands with opposite spin polarization, one occupied and one unoccupied, by strong Coulomb repulsion. The coupling between the  $3/2$  spin on the  $\text{V}^{2+}$  ion and the  $1/2$  spin on each  $(\text{TCNE})^-$  is proposed to be antiferromagnetic.

Due to its extreme air-sensitivity, preparation and measurements of  $\text{V}(\text{TCNE})_x$  in its non-soluble powder form [7] is cumbersome and this, together with its presumably structurally disordered nature (on the macro- and meso-scopic scale) has led to that the physical structure of the compound has remained un-known. Development of chemical vapor

deposition (CVD) fabrication techniques has however improved stability and reproducibility of the material [13-17]. An extended x-ray absorption fine structure (EXAFS) study has probed the *local* structure of the compound, showing that the vanadium ion coordinates to about six nitrogen atoms, most likely in a slightly distorted octahedral environment, each with an average distance in room temperature of 2.084(5) Å [18]. The small variation of V-N bond lengths in the local structure is also consistent with strong bonding, as required for magnetic ordering at relatively high temperatures.

As a result of the un-known physical structure of  $V(\text{TCNE})_x$ , theoretical calculations of the  $V(\text{TCNE})_x$  electronic structure have been impossible, but by using a model system of  $V(\text{TCNE})_x$ , namely alkali-doped TCNE, we have been able to partially circumvent this problem and theoretical results of alkali-doped TCNE have proven valuable in the interpretation of the experimental photoelectron spectroscopy (PES) and near edge x-ray absorption fine structure (NEXAFS) spectra of alkali-doped TCNE as well as of the more complex  $V(\text{TCNE})_x$  [12-14]. The first results on the occupied electronic structure were obtained from a study of the model compound  $\text{Rb}(\text{TCNE})$  [12] and have been compared with results on  $V(\text{TCNE})_x$  films that were prepared by a recently developed *in-situ* CVD method, enabling for the first time preparation *and* characterization of oxygen-free  $V(\text{TCNE})_x$  films [13]. The studies showed that there are strong hybridization between the vanadium and the TCNE in the occupied electronic structure. The strong hybridization between the TCNE and vanadium ions in the occupied electronic structure has also been modeled using ligand field multiplet (LFM) calculations and charge transfer multiplet (CTM) calculations in combination with NEXAFS and x-ray magnetic circular dichroism (XMCD) experimental data yielding an estimate of a hybrid  $V(3d)$ -CN highest occupied molecular orbital (HOMO) given by 60%  $3d^3$  and 40%  $3d^4L$ , where L is a hole on the cyano ligands [14]. Hence, the frontier occupied electronic structure is more complex than the previous proposed model [11] and the nature of

the unoccupied electronic structure is to date unknown. As a result of the complexity of the system, this is not only dependent on the size of the crystal field splitting between the  $t_{2g}$  and  $e_g$  orbitals of the V(3d) level but also on the so-called Coulomb-gap which is due to the small size of the TCNE-molecule and causes Coulomb-repulsion in  $V(\text{TCNE})_x$  [12]. The nature of the  $V(\text{TCNE})_x$  LUMO can be studied by NEXAFS, a method providing information about the unoccupied electronic structure in the presence of a core hole. The technique involves absorption of photons followed by excitation of core electrons to bound unoccupied levels. The measurements can be performed in different modes. In this work the sample is irradiated with synchrotron radiation and the photon energy is scanned over a certain interval while monitoring the intensity of emitted Auger electrons which is increased by an absorption event. By looking at the different absorption edges, as in the case of  $V(\text{TCNE})_x$ , C K-edge, N K-edge and V L-edge, respectively, it is possible to determine at which of the elements the different molecular orbitals have their density.

Herein we report on the unoccupied electronic structure of the organic-based magnet  $V(\text{TCNE})_x$  by studying pristine  $V(\text{TCNE})_x$  and Na-doped  $V(\text{TCNE})_x$  by NEXAFS in combination with PES.

## Experimental

$V(\text{TCNE})_x$  thin films were prepared in room temperature on sputter-cleaned gold substrates using a custom-built UHV-compatible deposition source based on chemical vapor deposition of bis(benzene)vanadium and tetracyanoethylene [13]. The background pressure in the preparation chamber was  $10^{-8}$  mbar. Na-doping was done *in-situ* at  $10^{-9}$  mbar range using an alkali metal source provided from SAES. The sodium was deposited in small steps in order to study the first changes in detail.

The thin films were studied *in-situ* using PES and NEXAFS at beamline I311 of the MAX-II storage ring at the synchrotron radiation facility MAX-lab in Lund, Sweden. The end-station is equipped with a SES-200 electron energy analyzer and the base pressure of the system is low  $10^{-9}$  mbar. NEXAFS was performed using the partial electron yield method. The energy calibration was performed such as errors of the monochromator and the analyzer was taken into consideration. In order to remove the background, all NEXAFS spectra were divided by a reference spectrum of sputter-cleaned gold, taken at C K-edge, N K-edge and V L-edge, respectively.

Additional PES measurements were performed in the home laboratory using a custom-built spectrometer equipped with a hemispherical analyzer. The base pressure of the system is  $10^{-10}$  mbar. For XPS measurements a non-monochromatized Al( $K_{\alpha}$ ) X-ray source at  $h\nu = 1486.6$  eV was used. The thin films of V(TCNE)<sub>x</sub> and Na-doped V(TCNE)<sub>x</sub> were prepared under the same conditions in the home laboratory as in MAX-lab.

## Results and discussion

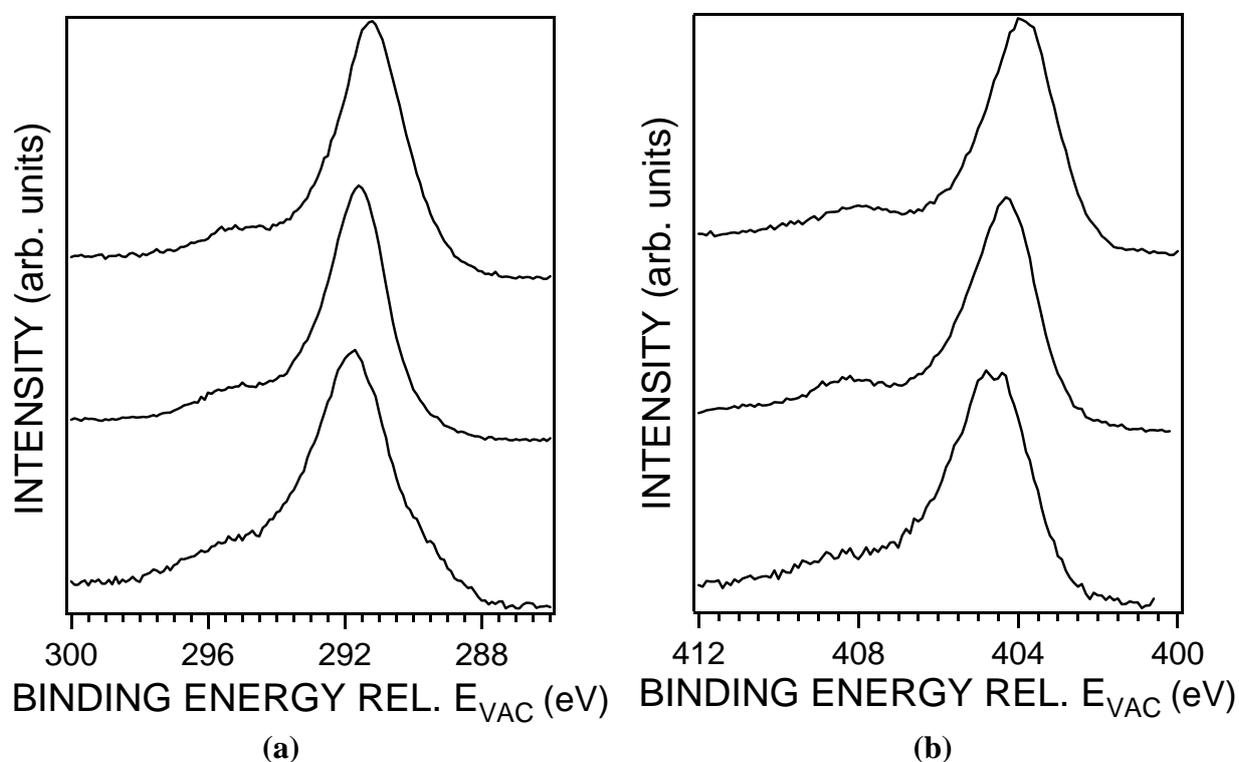
The evolution of the core level peaks, C(1s), N(1s) and V(2p), as well as N- and C-K-edge and V L-edge NEXAFS spectra were studied upon step-wise sodium doping of the organic-based magnet V(TCNE)<sub>x</sub>. There is simple charge transfer between the sodium atom and the V(TCNE)<sub>x</sub> system and no evidence for covalent bonding between sodium and V(TCNE)<sub>x</sub> is present in the spectra. More thorough discussions of pristine V(TCNE)<sub>x</sub> has been published earlier [13,14], but a short summary of each core level and each absorption edge is also given here for the convenience of the reader.

The C(1s) spectrum of un-doped V(TCNE)<sub>x</sub> (Fig. 1(a), bottom spectrum) has the main peak located at 291.7 eV relative to the vacuum energy level. At the higher binding energy side of the main peak there is a shake-up feature. A shake-up may arise upon the

photoemission process when the photon causes an electron to be emitted and hence creating a core hole. In order to screen the positive core hole the surrounding electrons are contracted (intramolecular relaxation). The contraction process also gives rise to “shock waves” of the electrons that can lead to an excitation of the molecule, a so-called shake-up process. In the one-electron picture, a shake-up event can be viewed as a core level ionization coupled to an e.g. HOMO to LUMO excitation. Since this excited state causes reduced kinetic energy of the emitted photoelectron, a shake-up feature typically is located a few electron volts higher in binding energy compared to the main photoelectron peak [19]. The small shoulder located at the low binding energy side,  $\sim 289$  eV, is intrinsic to all  $V(\text{TCNE})_x$  prepared by CVD technique, attributed to a bis(benzene)-related by-product [13]. In a previous study it has been shown that this feature increases upon air exposure [14]. As can be seen in the upper two spectra (Fig. 1(a)) the shake-up decreases as a consequence of step-wise Na-doping, which indicates that electrons are added into electron-accepting states with density on carbon units of the  $V(\text{TCNE})_x$  system. The main peak is shifted slightly towards lower binding energy upon Na-doping since the signal originates from a more electron rich environment than in the pristine  $V(\text{TCNE})_x$ . Moreover the residual bis(benzene)-related impurity disappears which indicates that it may work as a trap state [20] for electron transport. It is important to note that the impurity feature decreases earlier in the doping process than the shake-up, which means that the impurity states begin to be occupied by the injected electrons before the  $(\text{TCNE})^-$  states, i.e. the trap states are located at lower energy than the  $(\text{TCNE})^{2-}$  states.

The N(1s) core level of pristine  $V(\text{TCNE})_x$  (Fig. 1(b), bottom spectrum) is situated at 404.6 eV relative to the vacuum energy level, and analogous to C(1s) it has a shake-up at the higher binding energy side. On the higher binding energy side there is also an asymmetry, previously assigned to the fact that some nitrogen atoms must remain uncoordinated in the  $V(\text{TCNE})_2$  configuration since the vanadium ion only coordinates with up to six nitrogen

atoms while each TCNE molecule contains four [14]. The N(1s) peak does not have any impurity-related feature like the C(1s) counterpart, which supports the assignment of the trap state to bis(benzene)-related impurities. When the system is doped with sodium the shake-up decreases. This shows that the electron is added not only to an unfilled molecular orbital with density on carbon, but also to a molecular orbital with density on nitrogen, i.e. the charges from sodium are added to an unfilled molecular orbital with density on the TCNE molecular units of the  $V(\text{TCNE})_x$  system. Analogous to C(1s), the N(1s) peak is shifted towards lower binding energy upon increasing Na-doping.



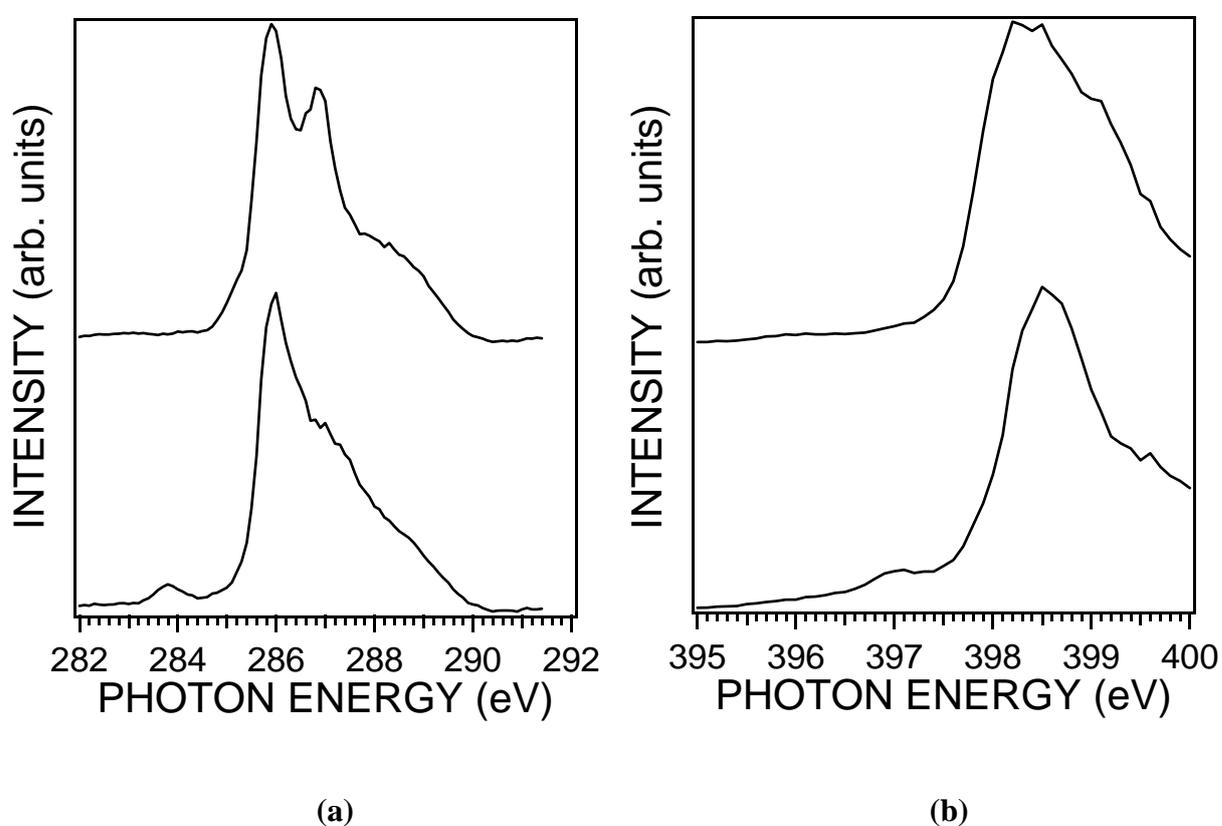
**Figure 1.** (a) C(1s) core level spectra upon increasing Na-doping, bottom spectrum corresponds to pristine  $V(\text{TCNE})_x$ . The number of sodium per carbon atom was calculated from atomic sensitivity factors (ASFs) to be 0.10 in the middle spectrum and 0.17 in the uppermost spectrum. (b) N(1s) core level spectra upon increasing Na-doping, bottom spectrum corresponds to pristine  $V(\text{TCNE})_x$ .

The V(2p) doublet peak (not shown here) is located around 520 eV (V(2p)<sub>3/2</sub>) and 527 eV (V(2p)<sub>1/2</sub>) relative to the vacuum level, respectively. From previous XPS and XAS studies the vanadium in V(TCNE)<sub>x</sub> is assigned to be in the V<sup>2+</sup> oxidation state [17,18]. In contrast to the C(1s) and N(1s) core levels, the V(2p) core level remains unchanged upon Na-doping, no energy shifts, new peaks or changes in intensity are visible. Since there are no discernible changes in the V(2p) spectra upon doping, the XPS results indicate that the by sodium added electrons end up in the (TCNE)<sup>-</sup>-units and not into the vanadium-derived states.

The C K-edge NEXAFS spectrum of pristine V(TCNE)<sub>x</sub> (Fig. 2(a), bottom spectrum) is summarized, from low to high photon energy, as follows. The absorption onset is a weak feature situated at ca 284 eV, corresponding to creation of a core hole and excitation into an unfilled molecular orbital with density on the carbon units. The next peak, the main absorption peak, is located at 285.9 eV and is broad at the high photon energy side, likely due to the structural disorder of the compound. This is in contradiction to pristine TCNE where the peaks are well-defined and more narrow [12]. When electrons are added to V(TCNE)<sub>x</sub> by Na-doping (Fig. 2(a), upper spectrum) the weak absorption onset feature at ~284 eV decreases and upon high doping it completely disappears, which strengthens the indications from the XPS measurements that injected electrons into V(TCNE)<sub>x</sub> are added to carbon atoms of TCNE, i.e. located in a molecular orbital with density on carbon. There are also changes between the doped and un-doped V(TCNE)<sub>x</sub> at the higher photon energy side of the absorption onset, but they are not discussed in detail here.

The N K-edge of V(TCNE)<sub>x</sub> (Fig. 2(b), bottom spectrum) has its absorption onset, i.e., excitation into an unfilled molecular orbital with density on cyano nitrogen, situated around 397 eV. The main absorption peak is located at 398.5 eV and as expected it is broad due to the structural disordered nature of V(TCNE)<sub>x</sub>. Upon Na-doping (Fig. 2(b), upper

spectrum), the weak feature at 397 eV decreases and in conjunction with the C K-edge results it is almost eliminated at high doping levels. The main peak appears broader and is slightly shifted towards lower photon energy. Since the nitrogen-derived absorption onset feature disappears upon doping, we can conclude that we not only add the by sodium injected electrons into carbon, but also into nitrogen, i.e. into an unfilled molecular orbital with density delocalized over the entire TCNE molecular unit.



**Figure 2.** (a) C K-edge of pristine  $V(\text{TCNE})_x$  bottom spectrum and Na-doped  $V(\text{TCNE})_x$  upper spectrum. (b) N K-edge spectra of pristine  $V(\text{TCNE})_x$  bottom spectrum and Na-doped  $V(\text{TCNE})_x$  upper spectrum.

The V  $L_{2,3}$ -edge of  $V(\text{TCNE})_x$  (not shown here) has two absorption peaks located at around 516 eV and 522 eV, respectively. Similar to the V(2p) core level the V  $L_{2,3}$ -edge NEXAFS spectra remains unaffected upon doping, no energy shifts, new peaks or changes in

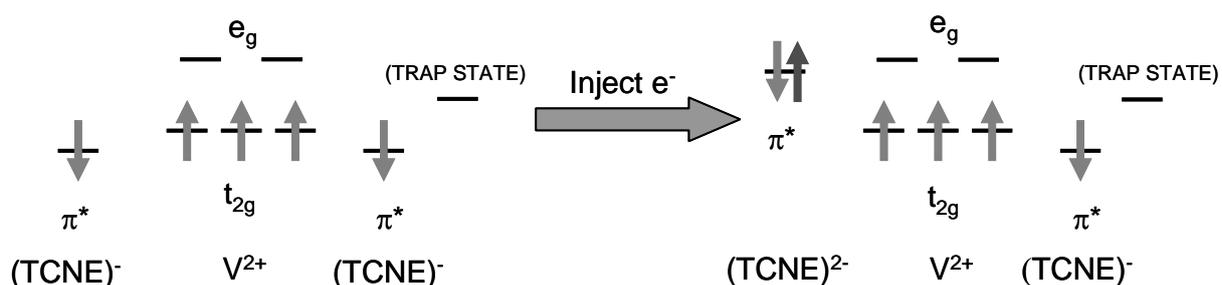
intensities are observable. Given that the V L<sub>2,3</sub>-edge remains unaffected upon doping this shows that no charges are added to the vanadium derived states upon Na-doping, i.e., we conclude that we add electrons to the (TCNE)<sup>-</sup> -units and not to the unfilled molecular orbitals with density on vanadium upon electron injection.

Hence from the combination of PES and NEXAFS it can be concluded that the electron accepting state of V(TCNE)<sub>x</sub>, i.e. the LUMO, is (TCNE)<sup>-</sup>-derived while the hole-accepting state, i.e. the HOMO, is hybridized and mainly localized on vanadium units as was shown in a previous study of the material [13]. This shows that the (TCNE)<sup>2-</sup> is located below the V(3d) e<sub>g</sub> orbital (see Fig. 3) since an electron is injected to the level which has the lowest energy and is in agreement with the model proposed by Prigodin, *et al* [11]. A simplified picture of the ground state of V(TCNE)<sub>x</sub> and of the configuration when an extra electron is added to the system is presented in Fig. 3. Note that there are additional states, as depicted in the figure, namely trap states, located below the (TCNE)<sup>2-</sup> energy level. Those states are primarily originating from byproducts from the reaction between bis(benzene)vanadium and TCNE, likely leading to increased disorder and decreased mobility of the material. It is important to point out that Fig. 3 presents a simplified picture of the electronic structure as there are significant hybridization of the HOMO as was shown from LFM and CTM calculations [14].

## Conclusion

In summary, we have characterized the unoccupied electronic structure of the organic-based magnet V(TCNE)<sub>x</sub> by NEXAFS and PES upon step-wise sodium doping. Simple charge transfer occurs between the V(TCNE)<sub>x</sub> and the sodium atoms and from the experimental data there is no evidence for covalent bonding or hybridization between sodium and V(TCNE)<sub>x</sub>. The electron-accepting state, i.e. LUMO, of V(TCNE)<sub>x</sub> is mostly localized on

(TCNE)<sup>-</sup> -units in contrast to the hole-accepting state, i.e. HOMO, which previously has been shown to mainly be V(3d)-derived [13]. There are also trap states present in the material, primarily originating from bis(benzene)-related by-products from the reaction between TCNE and V(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>, leading to increased disorder and hence decreased mobility of the material.



**Figure 3.** Proposed electronic structure of  $V(TCNE)_x$ . Ground state configuration and the configuration when one extra electron is added. As shown in the figure, there might also be some trap states in  $V(TCNE)_x$  originating mainly from bis(benzene)-related impurities from the reaction between bis(benzene)vanadium and TCNE. Note: This is a simplified picture, there is some hybridization between V(3d)-CN in the HOMO.

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